Sr partitioning in the benthic foraminifera *Ammonia aomoriensis* and *Amphistegina lessonii*

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ABSTRACT

The shallow water benthic foraminifera *Ammonia aomoriensis* and *Amphistegina lessonii* were grown at different seawater Sr/Ca and the test Sr/Ca ratio was determined by Laser Ablation - Inductively Coupled Plasma - Mass Spectrometry. *A. aomoriensis* test Sr/Ca is positively correlated with seawater Sr/Ca. The linear regression has a slope of 0.17, representing the overall Sr partitioning coefficient K_{DSr}. The slope remains unchanged, if seawater Ca concentration is changed in order to change the seawater Sr/Ca. In the case of *A. lessonii*, the slopes of the linear regressions representing K_{DSr} differ from one another i.e., 0.16 if the Sr concentration is changed and 0.32 if the Ca level is changed. This difference in K_{DSr} can be explained by the, relative to *A. aomoriensis*, high Mg content of *A. lessonii* (ca. 40 mmol/mol), distorting the calcite lattice and weakening the discrimination against Sr. The Mg content of *A. aomoriensis* is too low (ca. 4 mmol/mol) to observe the influence on Sr partitioning. All data are compatible with a recently developed model for minor element partitioning in foraminifera (Nehrke et al., 2013; Mewes et al., 2015a). On the whole, our data confirm the model (applicability of the model to Sr and dependence of the calcite Sr/Ca on seawater Sr/Ca, as opposed to seawater Sr concentration), and improve our understanding of the model (influence of calcite Mg/Ca on Sr partitioning).

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1. Introduction

The current climate change debate relies to a considerable extent on an understanding of climate change prior to human influence (Zeebe and Ridgwell, 2011; Martinez-Boti et al., 2015). Parameters such as past sea surface temperature are largely inferred from the chemical composition (the proxy values for the target parameters, e.g. temperature) of the fossilized tests of marine calcifying organisms (Nürnberg et al., 1996; Schifano, 1984; Takesue and van Green, 2004; Fenger et al., 2007; Ferguson et al., 2011; Ullmann et al., 2013; Schöne et al., 2011). A prime example of a group of organisms used as proxy archives is the foraminifera. Various species of this diverse group have proved to be of great value in the context of past climate reconstruction (Fischer and Wefer, 1999). The interpretation of geochemical proxies is challenging. For example, to estimate past water temperatures from oxygen isotopes of biogenic hard parts including foraminifera, requires knowledge of the $\delta^{18}O$ value of the ambient water (Grossmann and Ku, 1986; Spero et al., 1997). These complications in interpreting the isotopic and minor element composition (Elderfield et al., 2006) have sparked an interest in conceptual calcification models which explain trace element and isotope incorporation into biogenic skeletons, specifically foraminifera tests (e.g. Elderfield et al., 1996; Erez, 2003). Conceptual calcification models are mostly based on specific ideas about the transport of ions from seawater to the site of calcium carbonate precipitation. These models feature various modes of transport in different organisms, including extracellular bulk seawater transport in corals and molluscs (Gagnon et al., 2012; Crenshaw, 1972; Misogianes and Chasteen, 1979), and transmembrane transport in coccolithophores, dinoflagellates, corals, and molluscs (Langer et al., 2006; Gussone et al., 2010b; Taubner et al., 2012; Beniash et al., 1999; Suzuki et al., 2009; Addadi et al., 2006; Cuif et al., 2011). These studies show how concepts developed for one group of organisms might be used to explain minor element and isotope composition in another group. For instance the concept of transmembrane transport, common in coccolithophore literature, was used in some studies on dinoflagellates, corals and molluscs.

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It has recently also become influential in foraminifera research as detailed in the following.

Two main transport pathways for ions in foraminifera have been proposed, i.e. vacuolization of seawater (Elderfield et al., 1996; Erez, 2003) and transmembrane transport (Nehrke et al., 2013). Vacuolization of seawater alone delivers minor elements (all elements other than Ca) and calcium ions in the Me/Ca (Me = minor element) ratio they feature in seawater and thus leaves the entire partitioning to the calcite precipitation. This is an unlikely scenario, because compared to inorganically precipitated calcite many foraminifera produce calcite which is strongly depleted in magnesium (Mucci and Morse, 1983; Bentov and Erez, 2006; Raja et al., 2005; Mewes et al., 2014). Transmembrane transport of calcium mediated by transport enzymes and/or ion channels, by contrast, discriminates against magnesium (White, 2000) and can therewith explain why foraminiferal calcite in some cases is lower concentrated than inorganically precipitated calcite. Evidence for the importance of transmembrane transport comes from various independent observations, such as Mg isotopes of planktonic foraminifera (Pogge von Strandmann, 2008), Ca isotopes of benthic foraminifera (Gussone and Filipsson, 2010a; Gussone et al., 2016), U/Ca in *Ammonia* sp. (Keul et al., 2013), and proton efflux patterns during chamber formation in *Ammonia* sp. (Glas et al., 2012).

Transmembrane transport alone, however, cannot explain the large range of Mg/Ca ratios in different foraminiferal species (Bentov and Erez, 2006; Raja et al., 2005). In order to overcome these explanatory difficulties, conceptual calcification models include a combination of vacuolization and transmembrane transport. A seminal model assumes that vacuolization is the only source of Ca ions, but rather than simply using seawater, foraminifera were supposed to actively transport Mg ions out of the vesicle (Erez, 2003). This model was recently challenged by an alternative model (henceforth referred to as the "mixing model") which features transmembrane transport as the main source of Ca ions and assigns a modulating, but nevertheless important, role to seawater vacuolization (Nehrke et al., 2013). A refined version of this mixing model was shown to predict Mg-partitioning successfully at varying Mg/Ca ratios of seawater (Mewes et al., 2015a). Briefly, the mixing model features a total ion flux which is divided into passive transport (vacuolization or seawater leakage, PT, please note that vacuolization is not "passive" in physiological terms, i.e. it consumes energy) and transmembrane transport (TMT) (hence the term mixing model). Passive transport is characterized by no fractionation, whereas TMT is assumed to fractionate strongly against the minor element ion. The Mg/Ca$_{CC}$ ratio of the precipitated calcite is the result of the Mg/Ca ratio of these two fluxes. A premise of the mixing model is that Mg substitutes for Ca in the calcite lattice (Branson et al., 2013).

Given the above assumptions and the Mg/Ca ratio in seawater (R_{SW}), the mixing model describes the (Mg/Ca)$_{CC}$ (calcite Mg/Ca) by:

$$\left(\frac{Mg^{2+}}{Ca^{2+}}\right)_{CC} = R_{SW}\left[\frac{\text{frac}(1-x) + x + \text{frac} \cdot R_{SW}}{1 + (1-x+\text{frac}\cdot x)R_{SW}}\right] \qquad (1)$$

where x denotes the fraction of the total flux of the divalent cations (Mg^{2+} and Ca^{2+}) transported via PT and frac is the fractionation of TMT. From Eq. (1) it follows the partition coefficient for Mg (D_{Mg}):

$$D_{Mg^{2+}} = \left(\frac{Mg^{2+}}{Ca^{2+}}\right)_{CC}/R_{SW} = \frac{\text{frac}(1-x) + x + \text{frac}\cdot R_{SW}}{1 + (1-x+\text{frac}\cdot x)R_{SW}} \qquad (2)$$

The refined mixing model predicts that the Mg/Ca ratio of the test is positively correlated with the Mg/Ca ratio of seawater, regardless of whether the ratio is changed by changing Mg- or by changing Ca-concentration of seawater.

The original version of the refined mixing model assumes that the only fractionation step is transmembrane transport, but it was recently proposed that fractionation exerted by calcite precipitation plays a role

too (Mewes et al., 2015b). The present manuscript addresses two important issues left open by the previous studies. Firstly, we test the applicability of the mixing model to Sr fractionation. From the central idea of the model it follows that it should not only be applicable to Mg, but also to Sr. Secondly, we explain species-specific differences in Sr fractionation, which were noted by Mewes et al. (2015b), but not satisfactorily explained. We use two datasets for each species, *Amphistegina lessonii* and *Ammonia aomoriensis* respectively, one in which the Sr/Ca ratio of seawater was changed by changing the Sr concentration, and one in which the Ca concentration of seawater was changed. Seawater Ca concentration ranged from 3 to 34 mM, corresponding to a supersaturation of seawater with respect to calcite from ca. 1.5–17 (see also Mewes et al., 2015a). Seawater Sr concentration ranged from ca. 0.1–1 mM.

2. Material and methods

2.1. Foraminifera sampling and culture experiments

Specimens of the benthic intertidal foraminifer *Ammonia aomoriensis*, precipitating low Mg-calcite (test Mg/Ca = 0.4–4 mmol/mol), were sampled from the Wadden Sea near Dorumer Neufeld, Germany. Specimens of the tropical benthic foraminifer *Amphistegina lessonii*, precipitating intermediate Mg-calcite (40–60 mmol/mol) were sampled from a coral reef aquarium at Burger's Zoo in Arnhem, The Netherlands. Both species were kept in stock cultures in the laboratory (10 °C for *A. aomoriensis*, 25 °C for *A. lessonii*). Adult specimens were picked from the stock cultures and isolated in well plates, in which they reproduced asexually. Offspring were isolated and used for the culture experiments. All experiments were performed at 25 °C. The use of offspring ensured that all chambers analysed were grown under experimental conditions. Briefly, juveniles (2–3 chamber stage) were grown in Petri-dishes to adult size. The culture medium was exchanged every other day in order to ensure quasi-constant carbonate chemistry and avoid bacterial contamination (for details see Keul et al., 2013; Mewes et al., 2015a). Two different types of culture experiment were performed for *A. lessonii*, and one type for *A. aomoriensis*. In the first set of experiments on both *A. aomoriensis* and *A. lessonii*, the Sr concentration of the culture medium was varied by adding SrCl$_2$ (Merck, p.a. grade) to sterile filtered North Sea seawater (Helgoland) or, in the case of *A. aomoriensis* to artificial seawater (Kester et al., 1967). In the other set of experiments (*A. lessonii* only), the Ca concentration of the culture medium was changed by using a mixture of 70% artificial seawater and 30% natural North Sea seawater (for details see Mewes et al., 2015a). Adult specimens were harvested, rinsed in reverse osmosis purified water, dried at 60 °C in a drying cabinet, and analysed by means of LA-ICPMS.

2.2. Analyses of cultured foraminifera and culture media

Sample analyses were performed in different laboratories because of instrument availability. Details of the methods used in each laboratory are presented here.

2.3. Analyses of foraminifera tests by LA-ICPMS

2.3.1. Ammonia aomoriensis (varying Sr treatment)

A sector-field mass spectrometer (Element 2, Thermo Scientific) connected to an Excimer Laser (Lambda Physik), equipped with GeoLas 200Q optics was used to determine element concentrations and Sr/Ca ratios of cleaned foraminifera tests at Utrecht University (Reichart et al., 2003). The laser pulse repetition rate was set to 6 Hz, energy density at ~1 J cm^{-2} and ablation beam diameter at 80 μm. ^{24}Mg, ^{27}Al, ^{43}Ca ^{44}Ca, ^{55}Mn, and ^{88}Sr isotopes were measured and counts used to calculate elemental concentrations in the samples. A complete measurement cycle through all masses took 0.52 s. A glass standard (SRM NIST 610) was ablated three times (energy density ~ 5 J cm^{-2}) and an in-house matrix-

Table 1
Seawater (SW) and foraminiferal (CC) Sr/Ca and Mg/Ca including standard error (SE) and standard deviation (SD).

Sr/Ca$_{SW}$	Mg/Ca$_{SW}$	Sr/Ca$_{CC}$	Sr/Ca$_{CC}$ SE	Sr/Ca$_{CC}$ SD	Mg/Ca$_{CC}$	Mg/Ca$_{CC}$ SE	Mg/Ca$_{CC}$ SD	No. of specimens	No. of laser ablation spots
Amphistegina lessonii Sr variable (mmol/mol)									
8.6	5122	1.46	0.01	0.03	25.69	1.03	3.09	12	57
50.0	5091	8.64	0.14	0.41	22.19	0.70	2.10	12	53
78.5	5086	13.02	0.16	0.53	18.70	0.72	2.39	10	46
104.6	5074	17.12	0.17	0.72	17.51	0.57	2.33	11	49
Amphistegina lessonii Ca variable (mmol/mol)									
23.1	12,867	7.10	0.44	1.32	81.91	4.71	14.14	10	41
16.8	9318	4.60	0.13	0.39	70.71	3.83	11.49	12	48
12.0	6613	2.89	0.05	0.14	50.11	2.79	8.38	10	45
6.3	3399	1.25	0.04	0.13	28.22	1.49	4.71	11	53
3.2	1708	0.78	0.01	0.05	20.58	0.91	2.89	10	52
Ammonia aomoriensis Sr variable (mmol/mol)									
1.6	2802	0.25	0.01	0.02	8.14	2.12	5.18	6	30
34.5	4141	5.59	0.14	0.31	6.72	0.92	2.05	5	29
64.3	5629	11.06	0.60	1.35	7.38	0.94	2.10	5	27
97.1	5696	16.12	0.35	0.79	7.24	1.31	2.92	5	29

matched calcite standard once between every 10 samples. Using different intensities on glass standards versus calcite samples was shown not to affect the analyses (Dueñas-Bohórquez et al., 2011). 43Ca was chosen as an internal standard, assuming 40 wt% calcium in calcite, while counts for ^{44}Ca were used to check for consistency. Time resolved isotope counts during test ablation were integrated and the background subtracted using the data reduction software Glitter (version 4.4.3, Gemoc). Isotope counts were normalized to ^{43}Ca and concentrations were obtained relative to the measurements on the NIST standards (assuming standard natural isotopic abundances and values reported by Jochum et al., 2011).

2.3.2. Amphistegina lessonii (varying Sr and varying Ca treatments)

A Laser Ablation- inductively coupled plasma mass spectrometry (LA-ICPMS) system at the Department of Earth Sciences, University of Cambridge was used to determine Sr/Ca ratios of the foraminifera tests. This high-resolution depth profiling technique employs an Analyte G2 Excimer Laser (Teledyne Photon Machines Inc.) coupled with a Thermo i-CapQ ICPMS to measure trace element profiles through foraminifera shell walls. Sample preparation and analyses were carried out following protocols described in Eggins et al. (2003) and Sadekov et al. (2008). The Laser Ablation system was optimised for depth profiling by using a 40 μm ablation spot with 4 Hz frequency and 1.8 J/cm^{-2} laser fluence. The ICP-MS was optimised for maximum sensitivity across the Li-Sr mass range using NIST610 reference glass material, maintaining ThO/Th <0.5% and Th/U ratio ~ 1. The isotopes ^{7}Li, ^{11}B, ^{24}Mg, ^{25}Mg, ^{27}Al, ^{43}Ca, ^{44}Ca, ^{55}Mn, and 88Sr were measured, taking approximately 60–120 s to acquire each depth profile. Three to four profiles were generated from each foraminifera test and results from analyses of 10–15 tests used to obtain a representative average for each Sr experiment. Data reduction involved initial screening of spectra for outliers, subtraction of the mean background intensities (measured with the laser turned off) from the analysed isotope intensities, internal standardisation to ^{43}Ca, and external standardisation using the NIST-SRM610 glass reference material (Eggins et al., 2003). In-house eBlue and OKA calcite standards and NIST-SRM612 were used to monitor long term standard reproducibility which was Sr/Ca = 0.236 ± 0.0047(1SD) mmol/mol, 13.5 ± 0.78(1SD) and Sr/Ca = 0.416 ± 0.013(1SD) mmol/mol respectively.

All LA-ICP-MS profiles of each specimen were averaged and subsequently results from all specimens within a treatment were averaged. The results including the standard errors and standard deviations of the specimen averages are presented in Table 1.

2.4. Analyses of culture media by ICP-OES

2.4.1. Ammonia aomoriensis (varying Sr treatment)

Inductively coupled plasma optical emission spectrometry (ICP-OES; Iris Intrepid, Thermo Fisher Scientific Inc., USA) was used to determine the strontium and calcium concentrations of the diluted culturing solutions (1:100 for the high Sr, 1:0.10 for the low Sr-treatment). Ca^{2+} was measured at a wavelength of 318.8 nm, Sr^{2+} at 407.7 nm. Measurements were performed in triplicates and averages are reported here. Precision (% r.s.d) was better than 0.5% r.s.d determined by multiple measurements on the samples. A multi-element in-house standard was used for calibration, with Sr-ranging from 0.05 to 1 mg/l and Ca from 1 to 25 mg/l.

2.4.2. Amphistegina lessonii (varying Sr and varying Ca treatments)

Sr/Ca ratios of the *Amphistegina lessonii* culture media were determined by ICP-OES at the Department of Earth Sciences, University of Cambridge, exploiting the high precision capability of simultaneous ICP-OES for element ratio determinations (Schrag, 1999; de Villiers et al., 2002). Samples were run on a Varian Vista Axial ICP-OES using the 315.887 nm Ca and the 421.552 nm Sr emission lines. Calibration standards were prepared from IAPSO standard seawater, closely matching
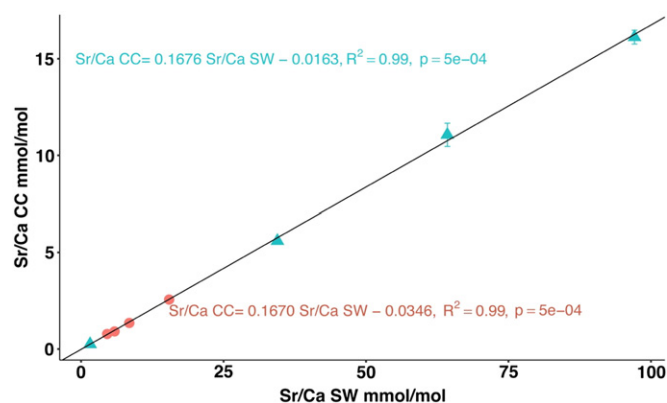

Fig. 1. Linear regression of Sr/Ca(cc) of *Ammonia aomoriensis* and Sr/Ca(sw). Blue triangles = experiment in which the Sr concentration of the seawater was changed, red circles = experiment in which the Ca concentration of the seawater was changed, data from Raitzsch et al. (2010). All LA-ICP-MS profiles of a specimen were averaged and subsequently all specimens within a treatment were averaged. Error bars represent standard error of specimen average. We give standard error and standard deviation of specimen average in Table 1.
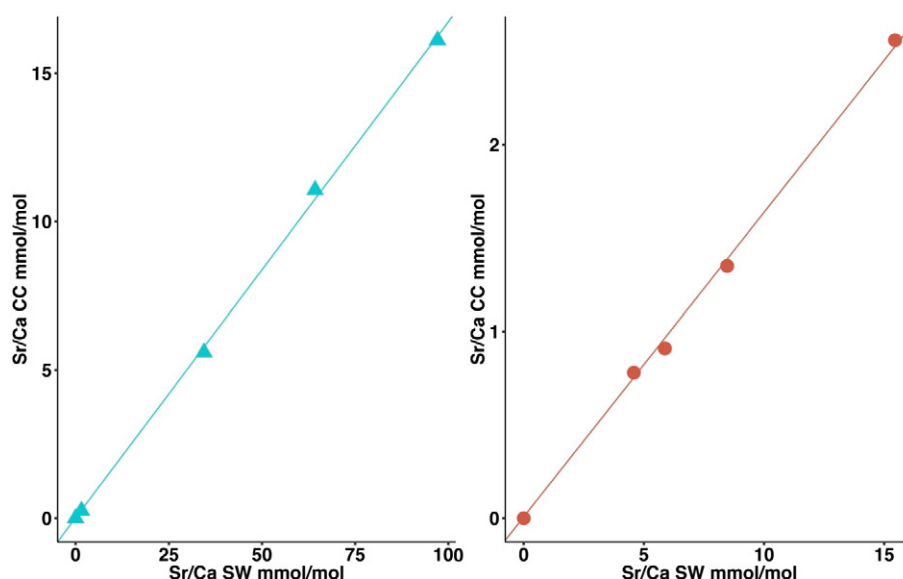
Fig. 2. Test Sr/Ca versus seawater Sr/Ca in *A. aomoriensis*. Blue triangles = experiment in which the Sr concentration of the seawater was changed (frac = 0.1644, see Introduction and Mewes et al., 2015a for model description), red circles = experiment in which the Ca concentration of the seawater was changed (frac = 0.1598, see Introduction and Mewes et al., 2015a for model description), data from Raitzsch et al. (2010). Lines represent the model fit (for detailed model description see Mewes et al., 2015a).

the major element concentration matrix of the media solutions, diluted to 110 ± 2 ppm Na and spiked with Ca and Sr to cover the concentration ranges in the experiments. Culture media solutions were diluted 100 fold, giving sodium concentrations of 100 ± 10 ppm and Sr/Ca ratios calculated from the measured concentrations. Instrumental precision was determined by replicate analyses of a consistency standard containing 16.2 ppm Ca and 1.08 ppm Sr (Sr/Ca = 30.6 mmol/mol) in an IAPSO standard seawater matrix with Na concentration of 108 ppm. Precisions of 0.83%, and 1.0% (r.s.d) were achieved for Ca and Sr concentration determinations respectively (n = 4), compared to a precision of 0.40% (r.s.d) obtained for Sr/Ca.

The partitioning coefficient of Sr (K_{DSr}) was calculated according to

$$K_{DSr} = (Sr/Ca_{CC})/(Sr/Ca_{SW}),$$

where (Sr/Ca_{CC}) = Sr/Ca of the foraminiferal calcite determined by LA-ICP-MS and (Sr/Ca_{SW}) = Sr/Ca of the culture medium determined by ICP-OES.

3. Results

We grew *A. aomoriensis* under different Sr concentrations and compare the test Sr/Ca versus seawater Sr/Ca relationship obtained from this experiment with the one presented in Raitzsch et al. (2010), where the Ca concentration was changed. In both cases the test Sr/Ca is positively correlated with the seawater Sr/Ca (Fig. 1). The slopes of the linear regressions are indistinguishable. These slopes represent the overall partitioning coefficients K_{DSr} for the two experiments. The refined mixing model (Mewes et al., 2015a) predicts these experimental results (Fig. 2). Both *A. lessonii* experiments, the Sr-variable and the Ca-variable, yield linear relationships between test Sr/Ca and seawater Sr/Ca (Fig. 3). The model predicts these relationships (Fig. 4). In contrast to *A. aomoriensis*, however, the slope obtained from the Ca-variable experiment is twice as steep as the one obtained from the Sr-variable experiment (Fig. 3). This is expressed in the different values for frac (Fig. 4).

In Fig. 5, the data of Fig. 3 are plotted in a different way. Here the regression lines are calculated for two groups of data points. Group 1 includes all data points which feature a test Mg/Ca < 30 mmol/mol, and group 2 includes all data points which feature a test Mg/Ca > 50 mmol/

mol (Fig. 5). Both groups are characterized by linear regressions with R^2 = 0.99. Please note that the slope of the Sr-variable experiment (Fig. 3) and the slope of the test Mg/Ca < 30 mmol/mol group (Fig. 5) are practically identical and that the slope of the test Mg/Ca > 50 mmol/mol (Fig. 5) is reasonably close to the slope of the Ca-variable experiment (Fig. 3). This reflects the fact that the test Mg/Ca and overall DSr are positively correlated (Fig. 6).

4. Discussion

We show firstly that K_{DSr} of *A. aomoriensis* does not depend on the Sr/Ca ratio of seawater, and secondly that the calcite Sr/Ca is positively correlated to the seawater Sr/Ca, regardless of whether seawater Sr concentration or seawater Ca concentration is changed. This behaviour of Sr mirrors that of Mg as predicted by the mixing model (Mewes et al., 2015a), which can consequently be used to calculate our experimental data (Figs 2, 4).
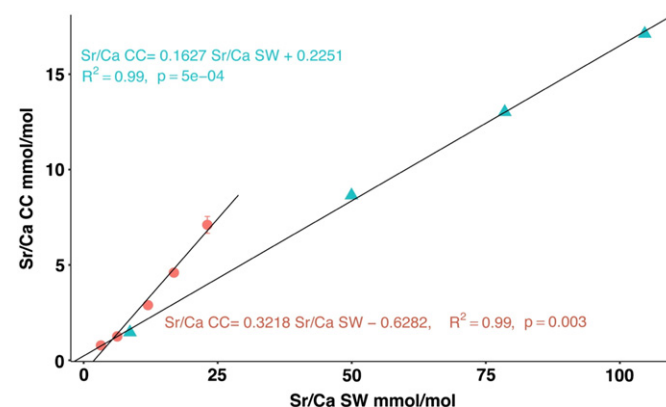

Fig. 3. Linear regression of Sr/Ca(cc) of *Amphistegina lessonii* and Sr/Ca(sw). Blue triangles = experiment in which the Sr concentration of the seawater was changed, red circles = experiment in which the Ca concentration of the seawater was changed. All LA-ICP-MS profiles of a specimen were averaged and subsequently all specimens within a treatment were averaged. Error bars represent standard error of specimen average. We give standard error and standard deviation of specimen average in Table 1.
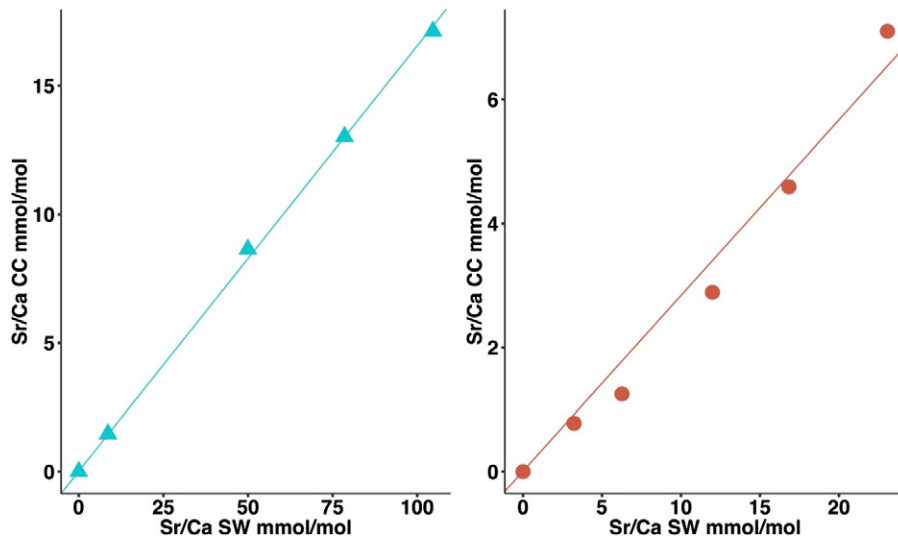
Fig. 4. Test Sr/Ca versus seawater Sr/Ca in *A. lessonii*. Blue triangles = experiment in which the Sr concentration of the seawater was changed (frac = 0.1625, see Introduction and Mewes et al., 2015a for model description), red circles = experiment in which the Ca concentration of the seawater was changed (frac = 0.2789, see Introduction and Mewes et al., 2015a for model description). Lines represent the model fit (for detailed model description see Mewes et al., 2015a).

Please note that the contribution of unfractionated minor elements equals 0.02 in all our calculations (the value was also used in Mewes et al., 2015a). This is mandatory when comparing the different experiments performed on one single species, because the contribution of unfractionated minor elements is assumed to be a species-specific parameter (Nehrke et al., 2013). For the same reason it is apparently inconsistent to use the same contribution of unfractionated minor elements for *A. aomoriensis* and *A. lessonii*. However, changing the contribution of unfractionated minor elements does not noticeably change the plots in Fig. 2, so we refrained from varying that number. The Sr-fractionation of transmembrane transport (frac in Fig. 2) in fact includes all processes that fractionate minor elements. Likely candidates dominating the parameter "frac" are transmembrane transport proteins such as ion transporters and ion channels, but also macromolecules in the calcifying fluid such as polysaccharides (Langer et al., 2006; Yuryev et al., 1979).

The fractionation exerted by calcite precipitation, however, can also contribute to the value of "frac". Previous studies did not precisely specify the processes contributing to "frac", but imply that transmembrane transport is the only site of fractionation (Nehrke et al., 2013; Mewes et al., 2015a). In a more recent study however it was suggested that fractionation exerted by calcite precipitation plays a role too (Mewes et al., 2015b), which is strongly supported by our data, as will be detailed in the following.

Changing seawater Ca concentration not only changes the seawater Sr/Ca ratio, but also the seawater Mg/Ca ratio and, as shown by Mewes et al. (2015a), the test Mg/Ca ratio. That means that the test Sr/Ca and the test Mg/Ca are positively correlated. In inorganically precipitated calcite Sr fractionation is influenced by the calcite Mg/Ca ratio (Mucci and Morse, 1983). A higher calcite Mg/Ca ratio causes stress in the crystal lattice which can partly be compensated by the incorporation of extra Sr, which results in a positive correlation between calcite Mg/Ca and the Sr partitioning coefficient. We propose that this effect is the basis for the weaker Sr fractionation in the Ca-variable experiment (Fig. 3). As a caveat it should be mentioned that an inorganic fractionation pattern in a biomineral does not necessarily point to an inorganic process underlying this pattern (Taubner et al., 2012; Keul et al., 2013; Gussone et al., 2016). However, a "mimicry" of an inorganic process
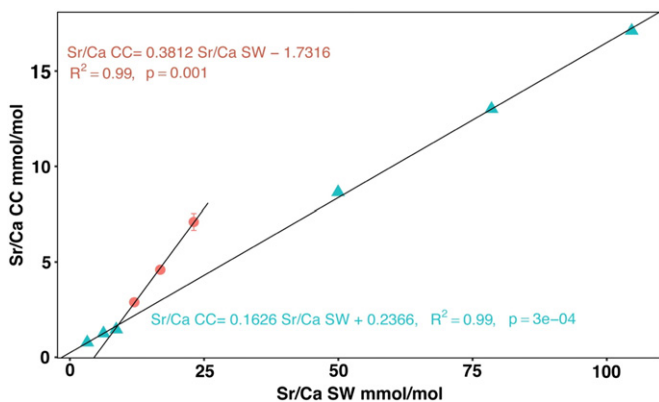

Fig. 5. Linear regression of Sr/Ca(cc) of *Amphistegina lessonii* and Sr/Ca(sw). Blue triangles = data from both experiments (Sr and Ca concentration of the seawater was changed). From the experiment in which the seawater Ca concentration was changed, only the tests containing <30 mmol/mol Mg/Ca are included. Red circles = experiment in which the Ca concentration of the seawater was changed. Only tests containing >50 mmol/mol Mg/Ca are included.
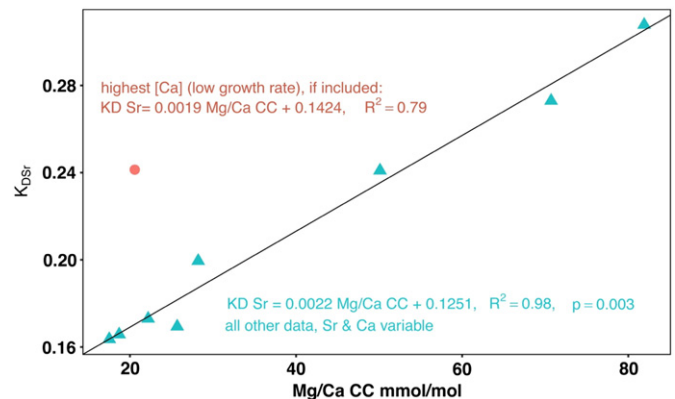

Fig. 6. K_{DSr} versus test Mg/Ca including linear regressions in *A. lessonii*. Blue triangles = data from both experiments (seawater Sr and Ca concentration changed), except the datapoint representing the highest seawater Ca concentration. Red circle = datapoint representing the highest seawater Ca concentration. This datapoint is characterized by a low growth rate of *A. lessonii* and might therefore feature altered physiological Sr fractionation.

by a physiological process (here TMT), would require that the site of this particular fractionation step in fact is not the crystal surface but the plasma-membrane. This is highly unlikely, because Sr fractionation depends on calcite Mg/Ca, not on seawater Mg/Ca, which is in contact with the plasma-membrane (Mewes et al., 2015b).

We will emphasize that this interpretation does not change when including the data point marked in red (Fig. 6). This data point corresponds to the highest seawater Ca concentration used in the Ca-variable experiment, i.e. 34 mM (as opposed to the 10 mM of normal seawater). This unnaturally high seawater Ca concentration had a detrimental effect on the growth rate of *A. lessonii* (Mewes et al., 2015a) and might have altered Sr fractionation through disturbed physiological processes.

At any rate, test Mg/Ca needs to be >30–50 mmol/mol in order to noticeably affect Sr partitioning. This test Mg/Ca seems to represent a threshold for the Mg/Ca effect on Sr partitioning as illustrated by an apparent non-linearity in the Ca-variable data, caused by the two lowest data-points (Fig. 3). This apparent non-linearity is absent when regrouping the data (Fig. 5). The low-Mg species *A. aomoriensis* by contrast features ca. 4 mmol/mol Mg/Ca (Mewes et al., 2014). The low Mg content of *A. aomoriensis* explains why the effect of Mg/Ca on K_{DSr} cannot be observed (Fig. 1; Raitzsch et al., 2010). It is interesting to note that Mewes et al. (2015b) report a positive correlation of test Mg/Ca and K_{DSr} in both *A. lessonii* and *A. aomoriensis*. The correlation for the latter species is weak ($R^2 = 0.08$) compared to that of the former ($R^2 = 0.6$) (Mewes et al., 2015b). Considering the data presented here, we can explain why this is so. It reflects the fact that *A. aomoriensis* contains too little Mg to measurably affect K_{DSr}. Therefore, the comparison of the K_{DSr} versus test Mg/Ca slopes of the two species as discussed in Mewes et al. (2015b) might have to be re-considered. Most likely, the slope for *A. aomoriensis* is not different from zero.

In summary, our data help to explain species specific differences in Sr partitioning of benthic foraminifera and improve the process-oriented understanding of the mixing model (Nehrke et al., 2013; Mewes et al., 2015a). While previous studies focused on the physiological components (transmembrane ion transport, vesicle ion transport) of the mixing model (Nehrke et al., 2013; Mewes et al., 2015a), it was hypothesised recently that inorganic precipitation might play an equally important role in the overall partitioning of Sr (Mewes et al., 2015b). Here we not only support this hypothesis, but also explain why the influence of inorganic precipitation can be seen in *A. lessonii* but not in *A. aomoriensis*. The Mg content of the latter species is so low that Mg does not effectively distort the calcite lattice to increase K_{DSr}. In *A. lessonii*, on the other hand, the relatively high Mg content substantially increases K_{DSr} and therewith reveals the role inorganic processes play in overall Sr partitioning of this species. Future biomineralization models for foraminifera should therefore combine physiological and mineralogical features in order to realistically capture the complex minor element partitioning of these organisms.

5. Conclusion

Both *A. aomoriensis* and *A. lessonii* display a positive correlation between seawater Sr/Ca and test Sr/Ca. However, the Sr partitioning behaviour of *A. lessonii* differs from the one of *A. aomoriensis*. The reason for this difference is the relatively high Mg content of *A. lessonii*, which leads to a weakened discrimination against Sr. The Mg content of *A. aomoriensis* is too low to measurably affect Sr partitioning. Nevertheless, a recently proposed model for divalent cation partitioning in foraminifera (Nehrke et al., 2013; Mewes et al., 2015a) is applicable to Sr partitioning in both *A. aomoriensis* and *A. lessonii*.

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